LOW-TEMPERATURE COAL DEPOLYMERIZATION. 5. CONVERSION OF NEW MEXICO AND UTAH HVB COALS TO HYDROCARBON OILS

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INTRODUCTION

The development of various low-temperature coal solubilization procedures, based on the application of selective chemical-catalytic reactions, has been reviewed in 1981 by Wender et al. (1) Such procedures have recently attracted considerable interest in view of the obvious advantages of coal liquefaction under mild, subsoftening conditions. In the preceding paper of these series, we outlined a new approach to low-temperature coal depolymerization and liquefaction which involves the application of three consecutive reaction steps in which different types of intercluster linkages are subjected to preferential cleavage (2). The procedure, as summarized in Figure 1, consists of the following sequential steps: (1) intercalation of the coal sample with catalytic amounts (3-15%) of $FeCl_3$ followed by mild hydrotreatment (HT) of the coal-$FeCl_3$ intercalate; (2) base-catalyzed depolymerization (BCD) of the product from step 1, under super-critical conditions; and (3) hydroprocessing (HPR) of the depolymerized product from the two preceding steps, using a sulfided CoMo catalyst. The high efficiency of the overall procedure was demonstrated by the previously reported conversion of a Wyodak coal sample into a light hydrocarbon oil product, containing 57.2 wt% (or 53.8 wt% calculated on the starting MAF coal) of low-boiling fractions (gasoline, kerosene and light gas oil; b.p. up to 305°C/760 torr). The present paper provides additional examples of the application of the same procedure, using two higher rank coal samples from New Mexico and Utah.

EXPERIMENTAL

Materials. Two HVB coal samples, one from Fruitland, San Juan basin (New Mexico) referred below as F(NM) coal, and another from the vicinity of Helper (Utah) referred below as H(UT) coal, were provided by Amoco Oil Co. The ultimate analysis of the F(NM) coal sample (MAF basis) in wt% was C, 78.69; H, 6,00; N, 1.62; Cl, 0.07; S, 0.96; O (diff.), 12.66; H/C = 0.909; ash content (dry basis), 11.37; BTU/lb (dry basis), 12,691. The ultimate analysis of the H(UT) coal sample in wt% was C, 81.10; H, 5.97; N, 1.09; Cl, 0.03; S, 0.49; O (diff.), 11.32; H/C = 0.877; ash content (dry basis) 9.91%; BTU/lb (dry basis), 13,111.

The coal samples were grinded and sieved through a 200-mesh standard sieve in a nitrogen-purged glove box, and then stored under nitrogen in a refrigerator.

Catalysts. The catalyst used in the mild HT step of the depolymerization procedure (Figure 1) consisted of $FeCl_3$, which was intercalated in the powdered coal feed using a newly developed procedure (see below). The catalyst-solvent system, used in the subsequent BCD step consisted of a 10% alcoholic alkali hydroxide solution, preferably a methanolic KOH solution (2). In the final HPR step the catalyst used was sulfided $6Co8Mo/\gamma$-Al_2O_3 prepared by incipient wetness impregnation of Ketjen γ-Al_2O_3 with an ammoniacal solution of ammonium paramolybdate, followed by impregnation with an aqueous $Co(NO_3)_2$ solution. This high Co content catalyst was

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found to be markedly more active for hydrodeoxygenation of depolymerized coal products and other oxygen-rich synfuels in comparison with conventional 3Co8Mo/γ-Al_2O_3 catalysts (3).

Apparatus and Experimental Procedure. Mild Hydrotreatment (HT) Step. Each of the powdered coal samples was first pre-extracted with THF in a Soxhlet for 48 hr, yielding small amounts of solubles, including resins (7.6% from the F(NM) coal, and 9.2% from the H(UT) coal). The pre-extracted coal was then intercalated with catalytic amounts (3-15% by wt) of reagent grade $FeCl_3$, using the following procedure:

About 20 g of the pre-extracted coal was accurately weighed and placed together with the desired amount of $FeCl_3$ into a 100 ml glass tube, connected to a previously described impregnation apparatus (4). About 20 ml of acetone was then added to the tube and the coal-$FeCl_3$-acetone mixture was stirred in an ultrasonic bath at room temperature for 1 hr. The excess acetone was distilled off under a stream of nitrogen and the resulting $FeCl_3$-coal intercalate was transferred to a porcelain dish and dried overnight in a vacuum desiccator oven at 60°C/0.02 torr.

3-4 g portions of the dry intercalate were hydrotreated in a specially designed autoclave system described elsewhere (2). Conditions used were: temperature, 250-270°C; hydrogen pressure, 1000-1500 psig; reaction time, 1-2 hr. In all runs the experimental procedure was the same as previously employed in the mild hydrotreatment (HT) of a Wyodak coal sample (2). The hydrotreated product was transferred to a Soxhlet and back-extracted with acetone to remove the $FeCl_3$ catalyst. Recovery of the latter was essentially quantitative (>99.5%) due to the low hydrotreatment temperature. The extracted product was subsequently extracted also with THF to recover a small amount (usually <10% by wt) of soluble products from the above HT step.

Base-Catalyzed Depolymerization (BCD) Step. The hydrotreated, $FeCl_3$-free coal product from the above HT step, in admixture with the above-mentioned small amount (<10% by wt) of solvent-free THF-soluble material, was subjected to BCD in a 150 ml autoclave, using a 10% methanolic KOH solution as depolymerizing agent. In all runs the amount of the hydrotreated coal feed was between 3-4 g, and the KOH solution/coal weight ratio was 10:1. The weighed coal sample and KOH solution were charged to the autoclave, and the latter was purged and then pressurized with nitrogen to an initial pressure of 1,000 psig. The autoclave was quickly heated (15°C/min) to the desired temperature in the range of 250-290°C, at which point stirring at 500 rpm was started and continued for 1 hr. With completion of the run the autoclave was quickly cooled down with water and depressurized. The product was transferred to a beaker and acidified with aqueous 2N HCl solution to pH = 2. The water-insoluble organic material was separated, thoroughly washed with distilled water, and finally dried in a desiccator at 100°C/0.2 torr. The dry product was then extracted with THF in a Soxhlet for 24 hr, leaving a solid residue consisting mainly of the original coal ash. In some experiments the solvent-free BCD product was fractionated into cyclohexane-solubles (oils), benzene-solubles, cyclohexane-insolubles (asphaltenes), and residual THF-solubles, benzene-insolubles (asphaltols), using a sequential procedure in which the total THF soluble, solvent-free BCD product was first extracted with benzene, and the resulting benzene-soluble fraction was freed from the solvent and then extracted with cyclohexane to separate it into oil and asphaltene fractions.

Hydroprocessing (HPR) Step. The total product from the sequential HT-BCD depolymerization steps (or in some experiments the oil fraction of the product) was subjected to hydroprocessing with a sulfided 6Co8Mo/γ-Al_2O_3 catalyst (see above), using a 300 ml stirred autoclave and mesitylene as a solvent.

In each run about 5 g of the depolymerized coal product was dissolved in 50 ml of mesitylene and charged together with 1 g of catalyst and several drops of CS_2 to the autoclave. The latter was purged with nitrogen, pressurized with hydrogen to an initial pressure of about 1500-1700 psig, quickly heated (15°C/min) to the selected reaction temperature (350-370°C), and then additionally pressurized with hydrogen to a reaction pressure of 2700 psig. The autoclave was stirred under these conditions for 4 hr, and then cooled down and depressurized. In some experiments the catalyst was exchanged at this point with a fresh catalyst portion (1 g) and the hydroprocessing repeated for another 4 hr. At the end of the run, the HPR product was quantitatively removed from the autoclave, separated by filtration from the catalyst, and analyzed.

Product Analysis. Depolymerized products from the sequential HT-BCD steps and the final hydrocarbon products from the HPR step were subjected to a combination of IR, C^{13} NMR, PMR and elemental analysis. The boiling point distribution of such products was determined by simulated distillation using a 18" x 0.25" stainless steel gas chromatographic column packed with 3% Dexsil 300 on Anakrom Q. A Hewlett-Packard, Model 5730 gas chromatograph was programmed for operation between -30° to 370°C at a rate of 11°/min (final temperature hold, 4 min; FID temperature, 400°C). Boiling point curves were calibrated with a standard mixture of C_9-C_{24} 1-phenylalkanes. GC data were fed directly, stored and calculated in a Hewlett-Packard 21MX E-series computer.

RESULTS AND DISCUSSION

Mild Hydrotreatment (HT) Step. Suitable conditions for mild hydrotreatment (HT) of the two $FeCl_3$-coal intercalates were first determined. This included determination of the optimal concentration of intercalated $FeCl_3$, the HT temperature, and the reaction time under which there is only partial breakdown of the coal framework by preferential cleavage of alkylene (e.g., methylene), benzyletheric, and some activated aryletheric intercluster linkages, with minimal (usually <10%) attendant solubilization (*2,4*).

Figure 2 shows the change in the yield of THF-solubles from mild HT (at 250°C) of the $FeCl_3$-F(NM) and $FeCl_3$-H(UT) coal intercalates as a function of $FeCl_3$ concentration. As seen, for the F(NM) coal $FeCl_3$ concentrations in the range of 8-12.5% by wt are sufficient for an HT step characterized by a desired, low-extent of solubilization (<10%). The slightly higher rank H(UT) coal, however, shows quite different behavior, as expressed in relatively much higher yields (ca 16-20%) at low $FeCl_3$ concentrations (5-10%) and markedly decreased yields of THF-solubles at higher $FeCl_3$ concentrations (15-20%). Figure 3 shows, however, that the yield of THF-solubles from HT of the $FeCl_3$-H(UT) coal intercalate can be brought down to the desired level (<10%) by decreasing the hydrotreatment time to about 1 hr (at 250°C). It is also seen in Figure 3 that increase in HT temperature to 290°C causes an excessive extent of solubilization which is undesirable from the point of view of the efficiency of the overall sequential depolymerization procedure. Specifically, the optimal conditions for the HT step were previously defined as those under which the extent of depolymerization and solubilization in the subsequent BCD step are maximal (see below) (*2*). Data summarized in Figure 3 show that low concentrations of $FeCl_3$ (5-10%) in the H(UT) coal intercalate are preferable to a higher concentration of this halide for HT at 250°C and 1-2 hr reaction time. On the basis of these results for the H(UT) coal a $FeCl_3$ concentration of 5% by wt, a temperature of 250°C, and a reaction time of 1-2 hr were selected as operating conditions for the HT of H(UT) coal. Figures 2 and 4, on the other hand, indicate that for the F(NM) coal a suitable set of HT conditions is a $FeCl_3$ concentration of 8-12.5%, a temperature of 250°C, and a reaction time of 1-2 hr. After removal of the intercalated $FeCl_3$ catalyst at the end of the mild HT step (see Experimental), the mildly hydrotreated F(NM) and H(UT) coals were subjected to base-catalyzed depolymerization (BCD), and the total yields of THF-soluble, depolymerized coal products from the sequential HT-BCD procedure determined (see below, Table 1).

Base-Catalyzed Depolymerization (BCD) Step. Table 1 summarizes the total yields of THF-soluble, depolymerized products from BCD of mildly hydrotreated F(NM) coal as a function of the temperature used in the preceding HT step. As seen, increase in HT temperature from 250° to 290°C results in gradual decrease in the yield of THF-solubles obtained in the BCD step (from 89.6% by wt for an HT temperature of 250°C to 68.0% for a temperature of 290°C). It is further seen that application of BCD alone to the same coal, without HT as preceding step (expt. 60) yields a markedly lower yield of THF-solubles (48.8%) as compared with that obtained by the combined HT-BCD procedure (compare with expt. 66 or 63), under otherwise identical BCD conditions. In experiment 66 the solubilization of the F(NM) coal is complete, as the insoluble residue left after the BCD step consists of the original coal ash only. Fractionation of the total THF-soluble product from the sequential HT-BCD processing shows that it consists mostly (>60% by wt) of cyclohexane-soluble (oil) components. In a series of comparative experiments, the conditions in the HT step were kept constant and identical with those in experiment 66, but the BCD step was performed at three different temperatures, i.e., 275°, 290° and 320°C. Fractionation of the products using solubility differences (see Experimental) showed that the oil fraction increases with increase in BCD temperature and becomes predominant at 290-320°C while the concentration of the combined asphaltene and asphaltol fractions reaches very low levels (<20% by wt). This behavior is consistent with previously reported results on the effect of BCD temperature upon the depolymerization of a Wyodak coal sample (*2*). It is also consistent with some earlier results which have shown that the product from base-catalyzed depolymerization of a Clear Creek, Utah coal at 320°C with NaOH-ethanol as depolymerizing agent consists predominantly of monocluster components(*5*).

Table 2 shows the change in the yield of THF-soluble products from BCD of mildly hydrotreated H(UT) coal as a function of BCD temperature in the range of 250-290°C, using otherwise identical conditions in both the HT and BCD steps. As seen, the total yield of THF-solubles increases with increase in BCD temperature from 37.0% (or 41.1% on the MAF coal) at 250°C to 72.6% (or 80.6% on the MAF coal) at 290°C. Complete solubilization of the H(UT) coal at 290°C requires extension of the BCD time to about 2 hr. It is also seen that BCD at 290°C without preliminary mild hydrotreatment (HT) of the coal (expt. 73) results in much lower solubilization yield (45.7%) as compared with that obtained by sequential HT-BCD (72.6%), using an identical temperature in the BCD step (expt. 74). Furthermore, the product from expt. 74 consists primarily (>60%) of cyclohexane-soluble (oil) components whereas the product from expt. 73 (without HT) contains only 21.8% of such components.

Hydroprocessing (HPR) of Depolymerized F(NM) and H(UT) Coals. Table 3 summarizes the elemental compositions of F(NM) and H(UT) depolymerized coal samples, as well as of products obtained from them in the last, i.e., the hydroprocessing (HPR) step of the sequential liquefaction procedure (Figure 1). As seen, the depolymerized coal samples retain the oxygen present in the starting coals, viz., the depolymerizing HT and BCD steps do not cause any appreciable extent of hydrodeoxygenation. However, structural studies based on C^{13} NMR, PMR and FTIR analysis of the products show that there is a major change in the oxygen functionality of the depolymerized coals as compared with the starting coals, i.e., most aryletheric and some dibenzofuranic intercluster linking groups undergo hydrolytic cleavage during the BCD step to yield phenolic groups (*6*). It is also seen in Table 3 that HPR of the depolymerized coals results in exhaustive hydrodeoxygenation, yielding hydrocarbon products of very low oxygen content. Structural analysis of HPR products and parallel model compound studies have elucidated the nature of some of the main depolymerizing reactions occurring in the HPR step, i.e., hydrogenolytic cleavage of condensed furanic rings (dibenzofuranic groups) and of Ar-Ar bonds (*3,6*). The reactions of such strong

Table 1

Yield of THF-Soluble Products from BCD of Mildly Hydrotreated F(NM) Coal as a Function of Temperature in the HT Step

Experiment, no.	60	66	63	61	62
HT step[a]					
Temperature, °C	--	250	250	275	290
$FeCl_3$ concentration	--	8.0	12.5	12.5	12.5
Yield of THF Solubles in HT Step, % by wt	--	6.0	6.7	8.6	14.8
BCD step[b]					
Temperature, °C	275	275	275	275	275
Total yield of THF-solubles, % by wt[c]	48.8	89.6	84.5	75.2	68.0
Insoluble residue[d]	51.2	10.4	15.5	24.8	32.0

[a]Initial H_2 pressure, 1500 psig; reaction time, 2 hr. [b]Initial N_2 pressure, 1000 psig; reaction time, 1 hr. [c]Total yield of depolymerized, THF-soluble products from sequential HT-BCD. [d]Including ash and non-depolymerized coal.

Table 2

Yield of THF-Soluble Products from BCD of Mildly Hydrotreated H(UT) Coal as a Function of the Temperature in the BCD Step

Experiment no.	71	72	74	73
HT step[a]				
Temperature, °C	250	250	250	--
$FeCl_3$ concentration, % by wt	5	5	5	--
Yield of THF-Solubles in the HT Step, % by wt	12.9	12.5	12.4	--
BCD step[b]				
Temperature, °C	250	275	290	290
Total yield of THF-Solubles. % by wt[c]	37.0	59.4	72.6	45.7
Insoluble residue[d]	63.0	40.6	27.4	54.3

[a-d]See corresponding footnotes a-d, Table 1.

Table 3

Elemental Composition of Depolymerized F(NM) and H(UT) Coals and of Hydrocarbon Products Derived from them in the HPR Step

	Depolymerized coal[a]		Hydroprocessed (HPR) product[b]	
Element, % by wt.	F(NM)	H(UT)	F(NM)	H(UT)
Carbon	77.71	77.35	88.38	88.97
Hydrogen	8.34	8.74	10.04	9.83
Nitrogen	0.93	0.50	0.35	0.21
Sulfur	0.14	0.11	<0.01	<0.01
Oxygen (by difference)	12.88	13.29	1.23	0.99

[a]The depolymerized F(NM) coal sample was obtained by HT at 250°C, followed by BCD at 275°C (see expt. 66, Table 1); the depolymerized H(UT) coal sample was obtained by HT at 250°C followed by BCD at 290°C (see expt. 74, Table 2).

[b]The hydroprocessing (HPR) of the depolymerized coals was performed at 370°C and 2700 psig H_2 pressure, using a sulfided 6Co8Mo catalyst and mesitylene as a solvent (for procedure, see Experimental).

Table 4

Boiling Point Distribution of Depolymerized F(NM) and H(UT) Coals and of Hydrocarbon Products Derived from them by Hydroprocessing (HPR)[a]

Fraction (b.p., °C) wt %	Depolymerized coal[b]		Hydroprocessed (HPR)[c] product	
	F(NM)	H(UT)	F(NM)	H(UT)
Gasoline (<200°)	5.0	1.1	18.0	18.7
Kerosene (200-275°)	3.5	4.2	35.5	27.2
Gas Oil (275-325°)	11.1	5.1	8.1	9.4
Heavy Gas Oil (325-400°)	9.4	6.9	7.2	7.7
Vacuum Gas Oil (400-538°)	12.7	5.7	10.6	13.9
Total Distillable (<538°)	41.8	23.0	79.4	76.9
Atmospheric Residue (>350°)	75.6	87.0	36.3	42.2
Vacuum Residue (>538°C)	58.2	77.0	20.6	23.1

[a]Boiling point distributions were determined by simulated distillation (see Experimental). [b]See footnote a, Table 3. [c]See footnote b, Table 3.

intercluster linkages involve as a first necessary step ring hydrogenation of at least one aromatic ring adjacent to the linkage, followed by C-O or C-C hydrogenolysis, respectively (*3,6*).

Table 4 summarizes the boiling point distribution of the depolymerized F(NM) and H(UT) coals, and of the hydrocarbon products derived from them in the HPR step. As seen, the oxygen-rich depolymerized coals are characterized by low volatility, as reflected in a total proportion of distillable components (<538°C) of 41.8% for the F(NM) coal and 23.0% for the H(UT) coal. The total proportion of gasoline- plus kerosene- range fractions is only 8.5% for the depolymerized F(NM) coal, and 5.3% for the depolymerized H(UT) coal. Hydroprocessing results in a dramatic change in volatility as reflected in a combined yield of 61.6% of low-boiling fractions (gasoline, kerosene, and gas oil; b.p. up to 325°C/760 torr) for the product from the F(NM) coal, and an yield of 55.3% of such fractions for the product from the H(UT) coal. Those results are similar to those previously reported for a lower rank Wyodak coal, and provide further support for the above outlined processing concept according to which preferential conversion of coals to light hydrocarbon oils requires in-depth, low-temperature coal depolymerization to monocluster products, prior to hydroprocessing.

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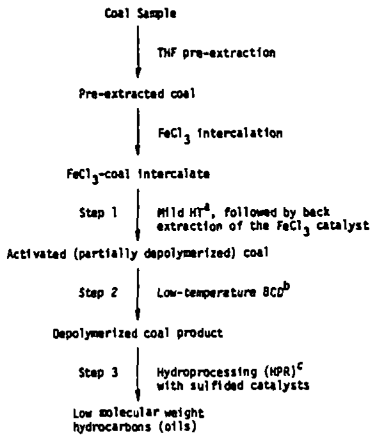

[a]HT = hydrotreatment (250-275°C; H_2 pressure, 1000-1500 psig)

[b]BCD = base-catalyzed depolymerization (250-285°C; initial N_2 pressure, 1000 psig)

[c]HPR = hydroprocessing (350-370°C; H_2 pressure, 2700 psig)

Figure 1. Low-Temperature Coal Depolymerization-Liquefaction Procedure.

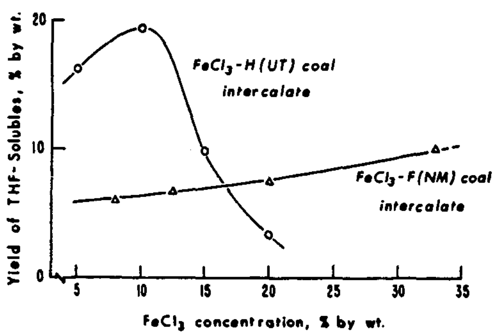

Figure 2. Yield of THF-Soluble Products from Mild HT of FeCl3-F(NM) Coal and FeCl3-H(UT) Coal Intercalates as a Function of $FeCl_3$ Concentration (250°C; 2 hr).

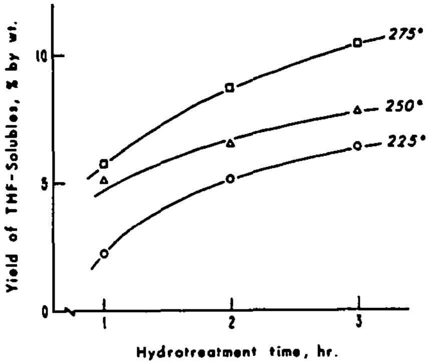

Figure 3. Yield of THF-Soluble Products from Mild HT of $FeCl_3$-F(NM) Coal Intercalate as a Function of HT Temperature(°C) and Time ($FeCl_3$ Concentration, 12.5% by wt.)

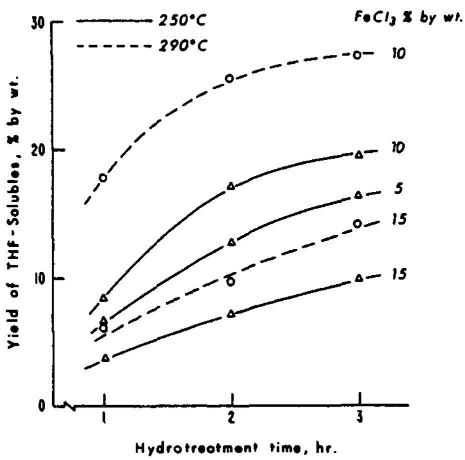

Figure 4. Yield of THF-Soluble Products from Mild HT of $FeCl_3$-H(UT) Coal Intercalate as a Function of $FeCl_3$ Concentration and Reaction Time.